

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.2-41 CRYSTAL STRUCTURES OF (-)-MALIC ACID AND OF A SECOND MODIFICATION OF (±)-MALIC ACID.

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(-)-Malic acid, in its ionized form, is one of the 4-carbon compounds that constitute the last stage of the citric acid cycle. Lenstra *et al.* [Doesburg & Lenstra, Bull. Soc. Chim. Belg. (1983) 92, 249; van Havere, Lenstra & Geise, Acta Cryst. (1980) B36, 3117, and references in these papers] have studied a series of salts of this biomolecule. The conformation of the malate ion appears to be dependent on the nature of the salt. Until lately no crystal-structure determination of malic acid was reported, presumably because of the difficulty in getting suitable crystals. Lenstra *et al.* [van Loock, van Havere & Lenstra, Bull. Soc. Chim. Belg. (1981) 90, 161] were the first to obtain single, albeit unstable, crystals of (±)-malic acid (I) suited to X-ray analysis. The space group is monoclinic, Aa , $Z=4$.

Unexpectedly, in a standard way (*viz.* by slow evaporation of an aqueous solution) we recently obtained good quality crystals of a second modification of (±)-malic acid (II) and of (-)-malic acid (III). Although the space groups of (I) and (II) are different, the cell constants are practically the same.

In all three crystal structures the molecules have a planar C-chain. They form extended chains with the carboxyl groups interlinked by H bonds into cyclic pairs. The aliphatic OH group in (I) is considered to be free, whereas in (II) and (III) it serves as a donor.

(±)- $C_4H_5O_5$ (II), $P2_1/c$, $a=4.889(1)$, $b=8.815(1)$, $c=13.036(2)$ Å, $\beta=102.93(1)^\circ$, $V=547.6$ Å³, $Z=4$, $\lambda(MoK\alpha)=0.7107$ Å, 774 unique reflections [$I > 2.5\sigma(I)$], $R=0.049$.
 (-)- $C_4H_5O_5$, $P2_1$, $a=5.041(3)$, $b=9.188(3)$, $c=11.792(5)$ Å, $\beta=94.06(4)^\circ$, $V=544.8$ Å³, $Z=4$, $\lambda(MoK\alpha)=0.7107$ Å, 553 unique reflections [$I > 2.5\sigma(I)$], current $R=0.042$.

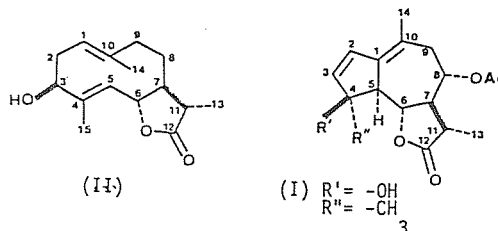
09.2-42 THE STRUCTURES OF ANION-RADICAL SALTS:

$C_2H_7N_2S$ -TCNQ AND $C_2H_7N_2Se$ -TCNQ.
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The crystal structures of a new series of TCNQ salts with S-methyl-thiuronium ($MT = C_2H_7N_2S$) and Se-methyl-selenouronium ($MS = C_2H_7N_2Se$) cations have been determined. X-ray diffraction data were collected on a Syntex $P2_1$ diffractometer with $MoK\alpha$ radiation. The structure was solved by Patterson methods, and full-matrix refinement was carried out using XTL program packages. Atoms S and Se were located by the heavy atom method. The remaining C, N and H were located by means of Fourier and difference Fourier syntheses. The compounds crystallise in the monoclinic space group $P2_1/c$ with: MT -TCNQ, $a = 11.005(2)$, $b = 12.305(3)$, $c = 11.112(3)$ Å, $\beta = 100.98(2)^\circ$, $v = 1482.2$ Å³, $Z = 4$, $D = 1.32$ gcm⁻³, final residual $R = 0.046$; MS -TCNQ, $a = 10.984(2)$, $b = 12.269(2)$, $c = 11.191(2)$ Å, $\beta = 100.94(1)^\circ$, $v = 1480.9$ Å³, $Z = 4$, $D = 1.53$ gcm⁻³, $R = 0.053$. The TCNQ ions are planar, the cyan-groups $-C(CN)_2$ being rotated by $4-6^\circ$ from the plane of the quinonoid ring. The bond length distribution in the TCNQ ions corresponds to the pseudo-aromatic type: all double bonds are lengthened by $0.51-0.53$ Å, and ordinary bonds are shortened. From the structures and bond distribution analysis the compounds are shown to be simple ion-radical TCNQ salts with full charge transfer and discrete anion pair stacking. The mean interplanar distance between TCNQ molecules is about 3.40 Å.

09.2-43 Structure and Conformation of a Stoichiometric Adduct of 4-Epimatricin with 3β-Hydroxydihydrocostunolide and of 4-Epimatricin alone.

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The guaianolide 4-Epimatricin and the germacrolide 3β-Hydroxydihydrocostunolide (I and II respectively) form in the solid state a stoichiometric non-covalent adduct through complex chain of hydrogen bonding involving their hydroxyl groups and one water molecule. 3β-Hydroxydihydrocostunolide exists in the solid state as a $\left[\begin{matrix} 15 \\ D_5 \end{matrix} , \begin{matrix} 14 \\ I \end{matrix} \right]$ chair-chair rotamer, whilst the cycloheptene ring of 4-epimatricin adopts a C_s conformation. Comparison of the crystal structures of the latter compound alone and in the adduct reveals a somewhat different conformation of the γ-lactone ring and a larger deviation from the ideal C_s symmetry of the cycloheptene ring in the adduct.